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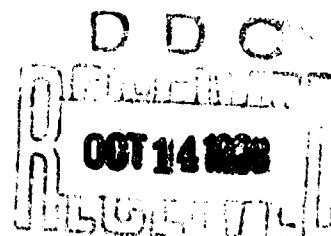
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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland



DETERMINATION OF THE SPECIFIC SURFACE OF SUBLIMATED
METALDEHYDE

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of Polymers)
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32-36

K. Biss and E. Kruecke

1. Preparation

The preparation, obtained by sublimation, was flaky, snow-like and typical for this type of sublimation(1). The flakes were placed on a glass slide, carefully covered with a cover slip in order not to damage the crystalline needles and sealed with Eukitt(2).

The first photomicrographs were taken with a Zeiss microscope and attached camera and they showed the crystals were heavily matted (Figure 1). With greater magnification, especially of crystals lying at the edge of the preparation, crystalline needles of uniform thickness, but highly variable length could be seen (Figure 2).

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Fig.1 see text



Fig.2 see text

2.Theory

In view of the heterogeneity of the crystals, it seemed difficult to determine directly the specific surface area, i.e. the surface area per gram of substance. Consequently, the following simplified model was postulated: the crystalline needles are cylindrical in shape and several times longer than wide, having the diameter d_s . In this case, the formula for the specific surface area becomes:

$$S_w = \frac{4}{Q \cdot d_s} \quad (Q = \text{density}) \quad (3,4) \quad [1].$$

When the edges were ignored, at least a portion of the diminished surface area, caused by the matting of the crystals, could be considered. The density of metaldehyde is said to be 1.27, according to Hassel and Mark(5), but 1.31 according to the crystal structure determined by Pauling and Carpenter(6). Our formula permits the determination of the specific surface by a single measurement of the thickness d_s of the crystalline needle.

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3. Microscopic Determination of Crystal Thickness

All photomicrographs were taken with an Orthomat microscope-camera combination (manufactured by E. Leitz, Wetzlar), equipped with a Fl. Apo Oil 90/1.15 objective, 90 X magnification, oil immersion, in a phase-contrast microscope with an arc lamp and a green filter. Total magnification was determined by photographing a stage micrometer, divided into 0.01 mm, with the same objective to 378.

Twenty-nine photographs were evaluated and the thickness of 335 crystalline needles was measured. A measuring microscope, Leitz TBS 50 (35 X magnification) was used, because of the small size of the diameter. The accuracy of three measurements, done each time, was about 3% and, in some cases, 5%. Since the thickness of the crystal surpassed the lateral melting tendency by about 0.30 micron, the photographs show typical, bright halos of weak phase contrast. Considering the unavoidable falsification of the picture (a weakness of the objective), the micrometer was always centered in the middle of the clear halo (7,8). On account of the axial melting ability of about 0.54 micron, only a portion of the crystal appeared sufficiently sharp under the microscope and suitable for measuring the thickness (compare Figures 3 and 4, taken in slightly different focal planes).



Fig.3 see text



Fig.4 see text

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Photographs taken in the center of the flaky preparation which was obviously strongly matted (Figure 5) showed that the thickness of needles there was similar to that of needles near the edge of the preparation (Figures 3 and 4). A tendency to form twin-needles and large aggregates can be seen in Figure 6. In such cases, only the thickness of a "single" was measured. Some needles had a length which extended over several microscopic fields.



Fig.5 see text



Fig.6 see text

The frequency histogram, shown in Figure 7, shows a maximum thickness of about 8×10^{-5} cm, i.e. 0.8 micron, and skewness towards increasing thickness. The locations of the minima and a second maximum at about 1.6 micron are noteworthy. The minima are discussed later on. The second maximum may have been caused by the inadvertent measurements of twin crystals which cannot be easily spotted, especially near the edges of the photomicrograph.

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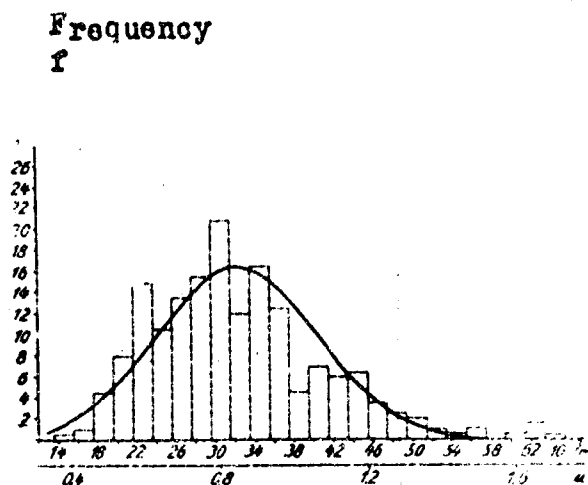


Fig. 7. Frequency distribution of thickness d_s of crystals (normal curve is shown for comparison)

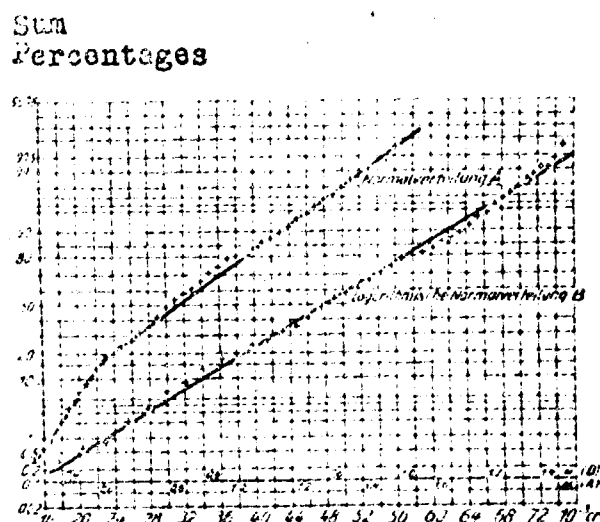


Fig. 8. Plotting the sum percentages on probability paper
A = normal distribution
B = logarithmic normal distribution

The calculation of the average gave $\bar{x} = 8.51 \times 10^{-5} \text{ cm}$, with a standard deviation of $\sqrt{\bar{x}^2/n} = 2.36$, or $2.14 \times 10^{-5} \text{ cm}$, depending on whether or not the second maximum at $1.6 \times 10^{-4} \text{ cm}$ was included. When the sum of percentages curve was plotted on probability paper, using either equidistant divisions (normal distribution) or logarithmic divisions (logarithmic normal distribution) neither approach showed complete agreement (Fig. 8). However, the observed distribution was better approximated by the logarithmic normal distribution curve (average $d_s = 8.0 \times 10^{-5} \text{ cm}$, standard deviation $= 2.0 \times 10^{-5} \text{ cm}$). By using the density value of 1.27 of Hessel and Mark (5) for metaldehyde and by applying formula (1), the specific surface was experimentally determined to be

$$S_w = \frac{4}{1.27 \times 8.51 \times 10^{-5}} = 3.7 \times 10^4 \text{ cm}^2/\text{g}.$$

4. Discussion

Although the length of the crystals showed considerable variability, the thickness was relatively uniform. Obviously, the growth in length was stronger than the growth in width. As soon as the needles reached a certain thickness, growth in that direction slows down, it seems, but continues in length.

Probably, the differential tendencies of growth rates with respect to different directions can be explained by the tetragonal crystal structure of metaldehyde. The space-centered elementary body with eight acetaldehyde molecules (space group C_{4h}^2) has the dimensions $a_0=b_0=10.40 \text{ \AA}$ and $c_0=4.11 \text{ \AA}$ (6,9)†

In this connection, it is of interest to note the recently discovered tendency of metaldehyde to form the nucleus in ice crystal formation (10). This tendency is shown by metaldehyde and nonisometric substances, e.g. silver iodide (at ordinary temperature), cobalt iodide and cadmium iodide.

Statistical results were of crucial importance because of the high variability of the crystalline needles in the preparation. As already mentioned earlier, the same thickness existed in the center and on the edges of the preparation of the needles.

If the irregularities of the decreasing portion of the frequency histogram are real, they may have been caused by not considering the length of the crystals. Beirne and Hutcheon (11) who examined the shape of coke particles also found similar deviations in their histogram. Coke is also a flaky particle (width and thickness about equal, but both much smaller than the length). Considering the "flakiness" (12) requires the additional consideration of crystal length. Formula [1] describes an idealized model of a cylindrical particle with a length much longer than the width and, actually, cannot be applied. The dimensions of the shape ought to be determined by independent measurements. Occasionally, variation in thickness may also occur among particles of average size.

The measured thickness of the crystals showed the relatively large deviation of about 25%. It must be assumed a modification of the method of sublimation (variation in the speed of the process, variation in the difference of the temperature of steam and condensing surface) may influence the tendency of growth in two directions on the part of the crystalline needles.

5. Summary

The specific surface of sublimated metaldehyde was determined microscopically on the basis of a simplified mathematical model and known density and was derived from the thickness of the crystals. The deviation of the distribution of crystal thickness from the normal curve was discussed. It was assumed that the tendency of metaldehyde to grow differentially in two directions at different rates was based on the nonisomeric crystal structure and was also influenced by the conditions of the sublimation method.

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